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MICROSCALE JOINTWARE

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MICROSCALE: A FEW WORDS

Recently, **microscale** laboratory equipment has appeared in the undergraduate laboratory and has materially changed some of the operations and equipment you'll be using. Pay attention:

1. **Microscale is small.** How small is it? Well there's no absolute cutoff, but some suggest 10 g is macroscale, 1 g is semi-microscale, and 0.1 g is truly microscale. Now 0.1 g of a **solid** is really something. A KBr (potassium bromide) infrared pellet uses 0.01 g (10 mg) and an NMR (nuclear magnetic resonance), taking five times as much (50 mg), leaves you with 40 mg to play with (melting point, chemical tests, hand in, and so on). Now 0.1 g of a **liquid** is really nothing. Liquids are difficult to divide; they, well, *flow*. And if you assume there're about 20 drops per milliliter for the average liquid, and the average liquid has a density of 1 g/ml, you've got two whole microscale drops. One drop for the IR, one for the NMR and for the boiling point... whoops!

Fortunately, most experimenters bend the scale so that you get close to 1g (approximately 1 ml) when you prepare a liquid product. *That does not give you license to be sloppy!* Just be careful. Don't automatically put your liquid product in the biggest container you have. A *lot* of liquid can lose itself very quickly.

2. **Microscale is new.** Not brand-spanking-new, but new enough that there's no real standardization on equipment. Or should I say there are several standards. I'm going with tradition, and sticking largely to the kinds of things described by Mayo, Pike, and Butcher in *Microscale Organic Laboratory*. These guys use real equipment with real ground-glass joints that often look vaguely like organic chemistry laboratory setups. Some just carry out lots of reactions in very long test tubes ("reaction tubes"), which is fine but not nearly as much fun.

I've put drawings of microscale equipment I've had occasion to use in this section, along with some discussion of the O-ring seals, conical vials, drying tubes, and so on. I've put full descriptions of certain microscale apparatus with the operations they're used in. So Craig tubes show up with recrystallization; the Hickman still is with distillation.

THE "O-RING CAP SEAL"

In the old days, you would put two glass joints together and, if you wanted a vacuum tight seal, you'd use a little grease. These days, you're told to use a plastic cap and and an O-ring to get a greaseless, high-tech seal. Maybe. Not all O-ring cap seal joints are created equal.

In a famous microscale manual, you're told how to make one of these seals between an air condenser and a conical vial from the top down. In sum:

1. Get a conical vial (appropriate size) that'll fit on the bottom end (male joint) of the wide-bottom air condenser (Fig. 31).
2. Drop the O-ring over the top of this air condenser.
3. Drop the cap over the top of this air condenser.
4. Carefully screw the cap down onto the threads of the vial.

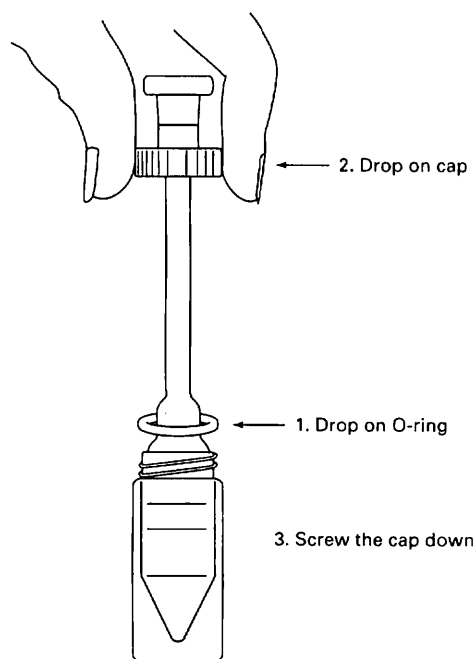


Fig. 31 O-ring cap seal on skinny apparatus.

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Unfortunately, you *can't* drop an O-ring and cap over a water-jacketed condenser, Hickman still, and so on. What to do? Using the water-jacketed condenser as an example, go from the bottom up:

1. Get a conical vial (appropriate size) that'll fit on the end (male joint) of the condenser (Fig. 32).
2. Take the vial **off** the end.
3. Put a plastic cap onto the male joint and hold it there.
4. Push an O-ring up over the male joint onto the clear glass. The O-ring *should* hold the cap up. (Fingers might be necessary.)
5. Put the conical vial *back* on the male joint.
6. Carefully screw the cap down onto the threads of the vial.

Sizing Up the Situation

As I said, microscale equipment design is in a state of flux, but there are a few things to note about the O-ring cap seal:

1. **A 3 to 5 ml conical vial and T 14/10 joints.** The plastic caps for these sizes have holes cut in them that are *extremely* tight. These

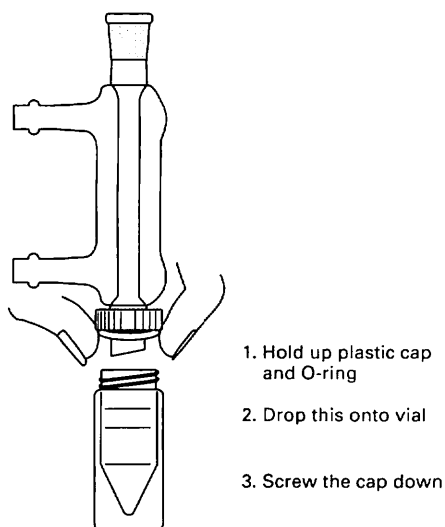


Fig. 32 O-ring cap seal on husky apparatus.

make a really good seal, and I suspect you would break the glass before *ever* pulling one of these babies apart. Once, when dismantling one of these joints, I caught the O-ring in the cap and as I pulled the cap off the joint, the cap sliced the O-ring in two. Watch it.

2. **A 0.3 to 1.0 ml conical vial and $\text{T } 7/10$ joint.** (Fig. 33) The T joint rattles around in the hole in the plastic caps for this size. As a consequence, whenever you tighten these joints, the O-ring squeezes out from under the cap. Yes, the joint's tight, but gas-tight? You can pull the joints apart with modest effort, and, if the O-ring has squeezed out entirely, forget the cap as a stabilizing force.
3. **A 0.1 ml conical vial and $\text{T } 5/5$ joint.** For these sizes, the hole in the cap is again snug around the male joint so that when you screw down the cap, the O-ring doesn't squeeze out. This joint also appears to be very tight.

Why I Don't Really Know How Vacuum Tight These Seals Are

I'll take a break here, and let Kenneth L. Williamson of *Macroscale and Microscale Organic Experiments* (D. C. Heath & Co., 1989), p. 102, take over. Here he is on the subject of Microscale Vacuum Distillation Assemblies: "On a truly micro scale (<10mg) simple distillation is not practical because of mechanical losses."

That's clear enough. You lose lots of your microscale product with a reduced-pressure (vacuum) distillation. As far as I know, no microscale laboratory manual has anyone perform this. Yes, you might be asked to

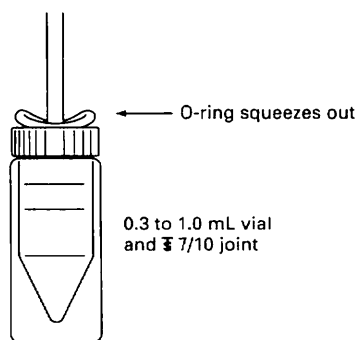


Fig. 33 O-ring squeeze-out with $\text{T } 7/10$ joint.

remove solvent under reduced pressure, but that's neither a reduced-pressure distillation nor uniquely microscale.

So, since nobody actually has any microscale reduced-pressure distillations, and with certain sizes of equipment the O-rings can squeeze out from under the plastic caps, and since I don't use them for reduced-pressure (vacuum) distillation anyway (I switch to a semi-micro apparatus with real 14/20 joints and—gasp!—grease), I don't know how vacuum tight these seals really are.

THE COMICAL VIAL (THAT'S *CONICAL*!)

The **conical vial** (Fig. 34) is the round-bottom flask of the microscale set, with considerably more hardware. When your glassware kit is brand new, every vial has a plastic cap, O-ring, and plastic disk to match. After one semester, every vial *needs* this stuff. When you check-in, make sure that every conical vial has a cap that fits and that you have at least one O-ring for each and a plastic disk that just fits inside this cap.

The Conical Vial As Vial

You would think that with an O-ring and a Teflon-faced plastic disk wedged under the cap, this would make a very tight seal. Think again. One of my

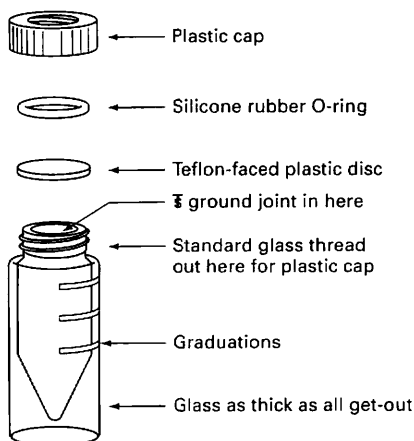


Fig. 34 The conical vial.

students made n-hexyl amine as a special project and packaged it in one of these vials; some of the amine leaked out, air got in, and the amine oxidized to a lovely brown color. You can still use these if you want but be careful:

1. Check to see that the Teflon-faced plastic disk doesn't have any holes in it. Sometimes you get to pierce a disk with a syringe needle in order to add something to a setup. You use the disk as a puncturable seal. With a puncture or two, the seal won't be as good as with a fresh disk. Just to be sure, get a new one if your disk has had lots of punctures.
2. The Teflon side to the chemicals, please. Especially if the compound might attack the plastic disk. Teflon is *inert*; the plastic is *ert*.
3. The O-ring goes close to the cap. Otherwise, it can't press the disk down to the glass.
4. Now the cap. Screw this baby down and you should, *should*, mind you, have a very well-sealed vial.

Laboratory Gorillas Please Note
Overtightening Caps Breaks the Threads
Thank You

Even so, watch for leaks! Sometimes you're asked to perform an extraction in one of these vials, and you decide to shake the bejesus out of the vial to get the two layers to mix. (See Extraction and Washing: Microscale.) After you clean your fingers, you *will* be more gentle when you repeat the experiment, won't you?

Packaging Oops

Did you get the weight of the product so that you could calculate the yield? ("What? *Calculation* in organic lab?") Fat lot of good that tight seal will do for you now that you have to undo it to weigh your product. And you'll lose a lot of your product on the walls of the vial. Nothing but problems. Especially in microscale.

Tare to the Analytical Balance

You can avoid losing your product and save a bit of time if you weigh the empty vial *before* you put your product in it. Microscale quantities, unfor-

tunately, may require a high-precision **analytical balance** rather than a **top-loading balance**, and you should be aware of at least one thing:

Analytical balances are very delicate creatures.

Only closed containers in the balance box!

Now I don't know if you have a hanging pan analytical balance with dialup weights or a fancy electronic model, and I don't care. Just keep your noxious organic products in closed containers, OK?

Electronic Analytical Balance

1. Open your notebook and, on one line, write "Mass of empty container," and get ready to write the mass in. What? You didn't bring your notebook with you to record the weights? You were going to write the numbers down on an old paper towel? *You fail*. Go back and get your notebook.
2. Turn the balance on. If it's already on, zero the balance. See your instructor for the details.
3. Open the balance case door, and put the empty vial with cap and O-ring and plastic disk on the balance pan. Close the balance case door.
4. Wait for the number to stop jumping around. Even so, electronic digital balances can have a "bobble" of one digit in the least significant place. Write down the most stable number.
5. Take the vial out of the balance case. *Now* fill the vial with your product. Close it up. No open containers in the balance case.
6. Write this new number down. Subtract the numbers. You have the weight of your product, with the minimum of loss.

"What if I have a **Tare bar** or **Tare knob**? Why not use this to zero the balance before putting in product. That way, I don't have to subtract—just get the weight of the product directly." Sure. Now take some of your product out of the vial to use in, say, another reaction. How much did you take? What? You say you already put it into the other reaction vial, and it's all set up and you can't take product out to weigh it? What? You say you think you'll lose too much product re-weighing it in yet another vial before you commit it to your reaction? Did you record the tare of the product vial? No? One subtraction too many for you, huh?

But if you did record the weight of the empty vial, cap, and O-ring, all you need do is remove some product, close the vial up, weigh it again, and subtract **this** weight from the sum of the tare and original product mass.

“What if I have a top-loading balance without a cage—do I have to have only closed containers on it while weighing?” Yes. Cuts down on the mess. An open container on a balance pan is usually an irresistible invitation to load product into it while on the pan, spilling the product onto the pan.

“What about weighing paper?” What *about* weighing paper. You *always* fill or empty your containers **away from the balance pan**, and you always weigh your samples *in these closed containers*, so what about weighing papers?

Heating These Vials

Sources of heat vary according to what you have available. Some use a can-type heating mantle, only it's filled with sand. You raise or lower the vial in the sand pile to set the temperature you want. Others use a **crystallization dish**, on top of a **hot plate with magnetic stirrer** (Fig. 35). You put the vial flat on the crystallization dish and add sand. You can monitor the temperature of the vial in a rough fashion by sticking a thermometer in the sand.

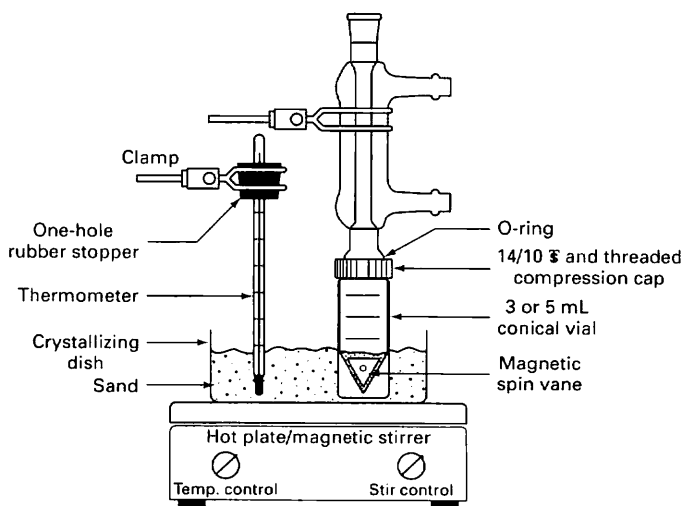


Fig. 35 Hot bath for conical vial; just happens to be a reflux.

THE MICROSCALE DRYING TUBE

The **microscale drying tube** (Fig. 36) is just a right-angled glass tube with a **T** joint on one end. You put a small cotton plug in first, and then load in the drying agent. Finish up with another cotton plug.

If you let these sit around too long, the drying agent cakes up and you could break the tube hacking this stuff out. It's actually cheaper to empty the tube after using it. If you can't hack that, soak the tube overnight (or so) and dissolve the caked drying agent out.

GAS COLLECTION APPARATUS

Several microscale kits have a **capillary gas delivery tube**. With this tube attached, you can collect gaseous products.

1. Put a cap on your **gas collection reservoir**. You can calibrate the tube by adding 2, 3, or 4 ml of water and marking the tube. Some have calibration lines. Check it out (Fig. 37).
2. Get a 150 ml beaker and fill it with water to about 130 ml. A 100 ml beaker filled to 80 ml will work, but it'll be a bit tight.
3. Now fill the **gas collection reservoir** with water, put a finger over the open end, invert the tube, and stick the tube (and your fingers) under the water. Remove your finger. See that the gas collection reservoir remains filled.
4. Angle the straight end of the **capillary gas delivery tube** under and into the gas collection reservoir (Fig. 38). Believe it or not, the gas

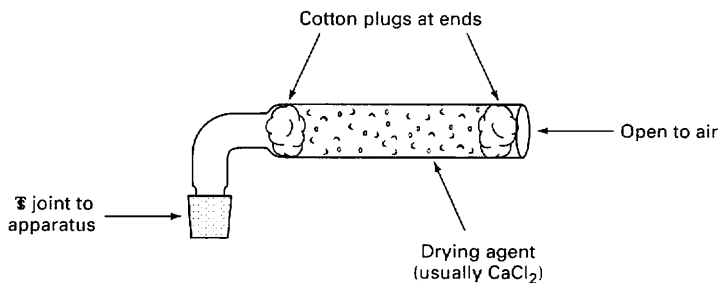


Fig. 36 A microscale drying tube.

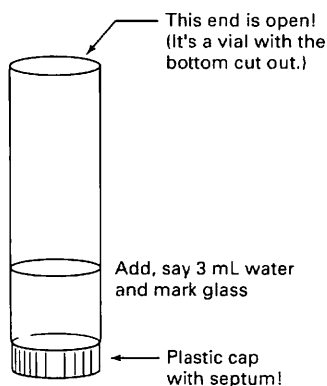


Fig. 37 Calibrating the gas collection reservoir.

collection reservoir, sitting atop the capillary gas delivery tube, is fairly stable, so you can put this aside until you need it.

5. When you're ready, use a ring with a screen to support the beaker at the right height necessary to connect the joint end of the capillary gas delivery tube to whatever you need to. Direct connection to a conical vial usually uses an O-ring cap seal; connection to a condenser may not (Fig. 39). Note that I've drawn the water connections to the condenser at an angle. Although the drawing is two-dimensional, your lab bench is not. You may have to experiment to find an arrangement that will accommodate the ringstand, hot plate, and other paraphernalia. Don't get locked into linear thinking.

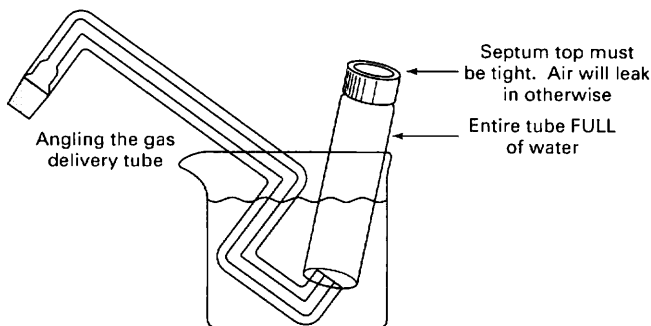


Fig. 38 Setting up for gas collection.

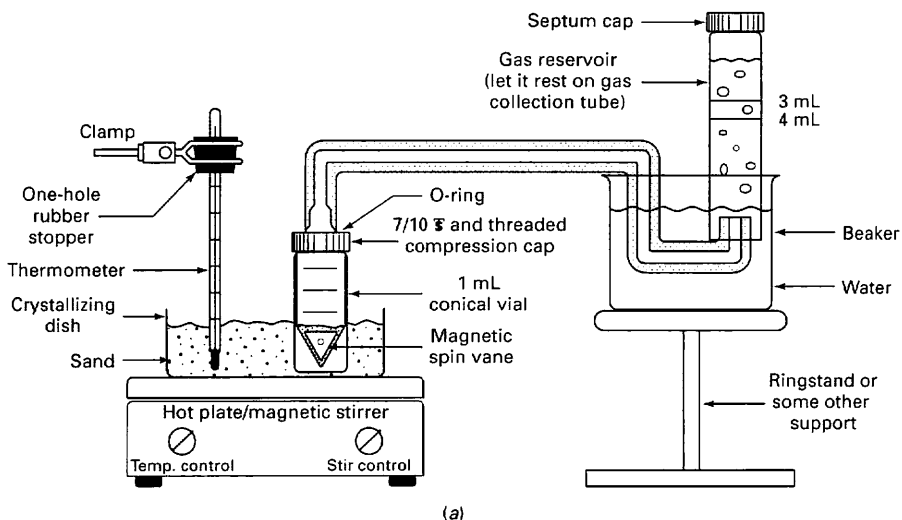


Fig. 39a Gas collection directly from a conical vial.

Generating the Gas

Usually, you warm the conical vial somehow to have the reaction generate the gas you want to collect.

Do not stop heating once you start!
Water will get sucked back into the reaction mixture
as the apparatus cools!

Watch the flow of gas into the collection bottle. If you increase the heat and no more gas comes out, the reaction is probably done.

Remove the capillary gas delivery tube first.
Then remove the heat.

Of course, some gaseous reaction product, a few microliters perhaps, will still come off the mixture. Don't breathe this. And you *did* carry this out in a hood, no?

If your capillary gas delivery tube was connected to the top of a condenser (Fig. 39b), just pick the beaker, collection vial, and capillary gas delivery tube up, as a unit, off of the condenser and set it down. Then attend to the reaction.

If your capillary gas delivery tube was connected directly to a conical vial with an O-ring cap seal (Fig. 39a), you have to undo the seal on a hot vial (!)

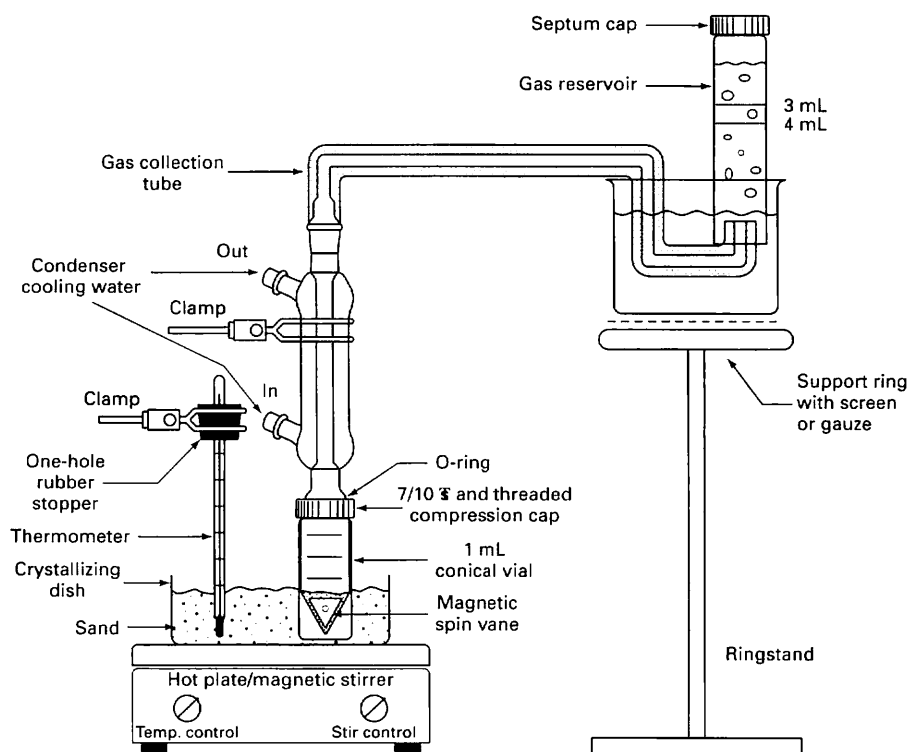


Fig. 39B Gas collection from a condenser.

in order to lift the entire system off as a unit. And you can't let the vial cool with the capillary gas delivery tube under water, or you'll get water sucked back into the vial. The best I've been able to do is carefully lift the gas collection vial off the gas delivery tube (Watch the water level in the beaker. If it's too low, the water in the collection vial will run out!) and then lower the beaker with the collection vial in it away from the capillary gas delivery tube. There's got to be a better way, but I don't know it yet. Ask your instructor.

Isolating the Product

With the **gas collection reservoir**, you have an O-ring cap seal with a Teflon-faced plastic insert. Pierce the insert with a hypodermic syringe and draw off some of the product. Usually, you put this gas through GC (see Chapter 30, "Gas Chromatography," for particulars).

Some Present-Day Gas-Collecting Ironies

Life in the organic laboratory does not usually present us with situations that have a modicum of wry humor, and when they occur they must be cherished. For instance none of the microscale kits sold by Ace Glass—the pioneers in this field—or its competitor, Corning Glass Works, includes the **gas collection reservoir**. It is sold separately, much as batteries are. Ace Glass Bulletin 898 has this beast in “typical undergraduate setups” on the cover, page 3, and page 5 in order to sell their microscale kits, but it’s not actually *in* any of their kits. *Caveat emptor*.

The usual capillary gas delivery tube has a $\text{F } 7/10$ joint—and we’ve seen that this size makes the least gas-tight seal. So, of course, it’s on the gas delivery tube. And some condensers don’t even *have* a thread on their $\text{F } 7/10$ outlet to tighten the cap on anyway. So much for greaseless gas-tight seals.

Finally, although I experimented a bit with this gas collection setup, mostly I read up on the technique in Mayo et al. By now they should have another edition out, but check the photo on the cover of the 1985 work: There it is—the entire gas collection setup in full-color glory—with the end of a Craig tube sitting on the capillary gas collection tube. I guess the batteries are extra even if you’re the group that designed the batteries.